

A Novel Method for the Determination of Gross Transuranic Activity in Uranium Compounds

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1. Overview

A Method to determine gross transuranic activity present in Uranium compounds and HP smears. From one count and one spectrum, three or more isotopes can be quantified. The method involves a simple digestion prep, sample extraction and precipitation. Results are obtained quickly with a very small expenditure on the part of the analytical lab.

2. Development

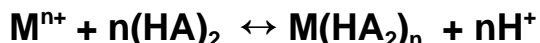
The method was developed to meet the requirements of a project bid presented to ASO in 1997. The project lasted one year, with samples submitted on a bi-weekly basis. Several methods were attempted to separate the U and Th from the Pu, Am, & Np. U-TEVA/TEVATM, ion exchange resins, and other extractions were examined. The methodology of the extraction was published by Nicolas Dacheux and Jean Aupiais in *Determination of Uranium, Thorium, Plutonium, Americium, and Curium Ultratraces by Photon Electron Rejecting α Liquid Scintillation*, Analytical Chemistry 1997, 69, 2275-2282.

3. Chemistry

- a. ALPHAEX _{α} TM is a non-polar organic extractant manufactured by ETRAC Laboratories. The complexing extractant is bis(2-ethylhexyl)phosphoric acid, or HDEHP.

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b. Equilibrium - The cation extraction by the HDEHP molecule is represented by the following equation:



c. Theory - According to Dacheux and Aupiais, with a V_{org} / V_{aq} ratio of 1 to 5, the extraction of various actinides is a function of pH in a variety of acid solutions.. D and A were interested in retaining the analytes of interest in the organic fraction, while ours was to remove what we didn't want with the organic phase. For our purposes, we needed to remove the U and Th and leave the remaining transuranics in the aqueous phase.

By examining the recovery graphs of D and A it was determined that U and Th were easily extracted from nitric acid solutions of molarities from $10E-5$ to $10E1$. At $10E-1$ molar nitric, Americium and Curium recovery fell to near 0%, while that of plutonium dropped to approximately 60%. D and A had outlined a method to sequentially extract U, Th, Pu, Am, and Cm using pH 1 nitric and a reducing agent. Since the HDEHP molecule preferentially binds actinides in oxidation states that are tetravalent or higher, the valence state of the plutonium at the time of extraction determines whether or not it will be recovered. By adding a mild reducing agent, ascorbic acid suggested by D and A, in 1mg/mL concentration we were able to retain most of the Plutonium and Neptunium in the aqueous phase .

c. Tracers - We traced this method using Pu-236 because the peak energy of this isotope is high enough that it does not interfere with Np-237, Am-241, Pu-238 or 239 which were our isotopes of interest.

4. Procedure

a. Flow chart - see handout

b. Method

The sample is digested.

An appropriate aliquot is taken.

The aliquot is evaporated and the residue is taken up twice in water to dispel any acid.

The residue is dissolved in pH1 nitric acid, 10mL and transferred to a glass vial

The sample is heated, then 100uL of 1g/mL ascorbic acid is added

The sample is allowed to sit at room temp for ~ 45 minutes

2mL of the extractant is added to each sample vial and the vials are placed on a shaker for 5 minutes.

The vials are centrifuged at <1000 rpm for ~3 minutes then the organic phase is removed with a disposable transfer pipette.

Organic phase may be retained if analysis on U or Th is desired

Take aqueous phase to dryness

Digest residue with conc. Nitric acid and H_2O_2

Bring up cleaned sample in 2-4M HCL (~15mL)

Add 1 mL of 3M sodium nitrite and transfer to plastic centrifuge tube

Incubate samples for ~45 minutes

Proceed with NdF3 precipitation

c. Cost - For our lab, the supply/reagent cost per sample is around \$5. We use the following items per sample for preparation:

supplies:

- 2 50mL beakers
- 2-6 disposable transfer pipettes
- 1 glass extraction vial, 6 dram (poly lid)
- 1 alpha planchet
- 1 Polypropylene filter (0.5 micron)
- 1 Polypropylene centrifuge tube
- 5-6 pipette tips

reagents:

- 10 mL pH 1 nitric acid
- 5-10 mL concentrated nitric acid
- 2-5 mL 30% hydrogen peroxide
- 100uL 0.15g/mL ascorbic acid
- 1 mL 3M sodium nitrite
- 15 mL 2-4M hydrochloric acid
- 100uL 0.05mg/mL neodymium chloride
- 2-3mL concentrated hydrofluoric acid
- 4 mL ALPHAEX_α

equipment:

- pipettor
- mechanical shaker
- hotplate
- vacuum filtration system

5. Data review

The areas of interest can be summed together and reported as gross TRU activity, or if multiple tracers have been used, each area can be summed from the single spectrum.

6. Troubleshooting

a. Tracing - It would be advisable to add Am-243 as well as the Pu-236, this traces the Americium while the Np-239, which is a daughter of the Am-243 can be counted by GFPC for beta activity to trace the Np. Cm-244 could be used if both Am-241 and Am-243 were to be reported.

b. Recoveries - Plutonium and Neptunium are variable, because of the valence instability. Americium and Curium recover much more reliably.

c. Uranium/Thorium - If desired U and Th can be recovered from the organic phase by back extraction with sulfuric acid. The aqueous fraction can be dried down and cleaned, then the fraction can be processed through separation chemistry to generate two sample preps to count by alpha spectrometry.

7. Conclusion

This method was developed as a quick and inexpensive way to determine gross TRU activity in Uranium samples. Currently, it is being used to provide quick turnaround results for Health Physics smear analysis. We are continuing to pursue modifications of this method which will allow us to determine more information about radioisotope levels in samples submitted to our laboratory.

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